

Title: Hexanuclear and undecanuclear iron(III) carboxylates as catalyst precursors for cyclohexane oxidation

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Abstract: Two multinuclear complexes [Fe-6(μ (3)-O)(2)(μ (4)-O-2)L-10(OAc)(2)(H₂O)(2)]center dot 2.625Et(2)O center dot 2.375H(2)O (1) and [(Fe11Cl)-Cl-III-(μ (4)-O)(3)(μ (3)-O)(5)L-16(dmf)(2.5)(H₂O)(0.5)]center dot Et₂O center dot 1.25dmf center dot 3.8H(2)O (2), where HL = 3,4,5-trimethoxybenzoic acid and dmf = dimethylformamide, have been prepared from trinuclear iron(III) carboxylates via their structural rearrangement in dimethylformamide or diethyl ether-dimethylformamide 9:1, respectively, and slow vapor diffusion of diethyl ether into the reaction mixture. Both compounds have been characterized by X-ray diffraction, optical, Mossbauer spectroscopy, and magnetic measurements. Complex 1 possesses a hexanuclear ferric peroxido-dioxido {Fe-6(O-2)(O)(2)}(12+) core unit, which adopts a recliner conformation, while complex 2 contains an unprecedented {Fe11O8Cl}(16+) core, in which 9 ferric ions are six-coordinate and the remaining two are five-coordinate. Another structural feature of note of the undecanuclear core is the presence of a deformed cubane entity {Fe-4(μ (3)-O)(μ (4)-O)(3)}(4+). Both complexes act as catalyst precursors for the oxidation of cyclohexane to cyclohexanol and cyclohexanone with aqueous H₂O₂, in the presence of pyrazinecarboxylic acid. Remarkable TONs and TOFs (the latter mainly for 1) with concomitant quite good yields have been achieved under mild conditions. Moreover, 1 exhibits remarkably high activity in an exceptionally short reaction time (45 min), being unprecedented for any metal catalyzed alkane oxidation by H₂O₂. The catalytic reactions proceed via Fenton type chemistry.

KeyWords Plus: Single-pot hydrocarboxylation; Mild Peroxidative oxidation; Nonheme iron catalysts; Copper triethanolamine complexes; Hydrogen-peroxide Crystal-structure; C-H; Alkane hydroxylation; Highly efficient; Metal-free

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